

# Monte-Carlo Model for the Hydrogenation of Alkenes on Metal Catalyst

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**ABSTRACT:** A Monte-Carlo model for the simulation of alkene hydrogenation on metallic catalysts has been developed and implemented in Fortran language. We describe the model employed for ethylene hydrogenation on platinum and show the flow chart of the program. Computational characteristics such as number of necessary calculations to reach steady state, running times on different platforms, and effect of the size of the catalyst matrix, are presented. Good correlation between simulated and experimental data was observed. A subroutine allows for visual observation of the reaction. This approach is very useful for obtaining a personal impression of the important factors governing the reaction. By using this example the advantages of Monte-Carlo simulation to test the level of understanding of catalytic phenomena are discussed. © 1998 John Wiley & Sons, Inc. *J Comput Chem* 19: 396–403, 1998

**Keywords:** Monte-Carlo simulation; catalytic processes; stochastic kinetic model; solid surfaces; graphic representation; catalysis by metal

## Introduction

This paper shows that a very simple model of the elementary events taking place in heterogeneous catalysis is sufficient to develop a Monte-Carlo (MC) model, in order to explain experimental results. It is possible to run such a simulation

on a personal computer (PC), so the procedure can be widely applied for testing various hypothesis and understanding laboratory data.

Interpretation of kinetic and mechanistic studies of heterogeneous catalytic processes requires deep insight into the microscopic events. One of the possible approaches to test various hypothesis is MC modeling. This treatment has been suggested for heterogeneous catalytic reactions,<sup>1</sup> because the other alternative, solution of the differential equa-

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tion system resulting from the set of postulated reactions, has very strong limitations. The use of MC simulation is popular in studies on diamond growth,<sup>2,3</sup> but it has also been used in theoretical studies,<sup>4,5</sup> as part of general treatment of hydrocarbon reactions,<sup>6</sup> and in investigations on the practical aspects of catalytic reactions, e.g., CO oxidation on Pd—Sn catalyst.<sup>7</sup>

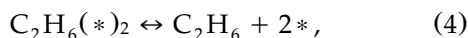
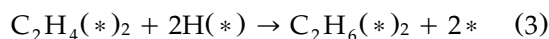
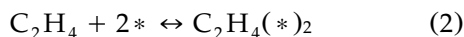
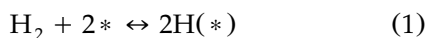
In many cases the probabilities needed for the MC simulation have been derived from molecular dynamics or transition-state-theory calculations<sup>3,6</sup> or have been based on analogy with experimentally determined rate constants.<sup>2</sup> Thus, with the exception of a very few cases,<sup>4</sup> very detailed background knowledge has been required, which obviously limited the application of MC simulation to the field of heterogeneous catalysis, where such data are not abundant.

To make the MC simulation technique applicable for a wide range of catalytic processes, one has to find suitable methods to utilize macroscopic laboratory data (such as selectivity or turnover frequency), without the need for microscopic data (such as MD simulation or rate constant values of elementary reactions). In this paper we show that this approach is indeed feasible and describe the applied computational procedure in detail. We use ethylene hydrogenation on platinum as an example, but the same method could be applied to most catalytic processes.

The MC technique lends itself easily to visualization of the catalyst surface during the reaction. As an additional advantage, such a tool proved to be effective in obtaining a very instructive picture of the important aspects of the reaction.

## The Chemical Model

The chemical model has been described in detail in our previous work.<sup>8</sup> The following chemical processes are taken into consideration:



where \* and (•) represent empty and occupied catalyst sites, respectively, and  $X(*)_n$  is a generic species  $X$  occupying  $n$  adjacent catalyst sites.

Steps 1, 2, and 4 are the (reversible) adsorption-desorption steps for hydrogen, ethylene, and

ethane, respectively (adsorption of ethane is nevertheless neglected in the calculation owing to its low concentration in the gas phase). Hydrogen is dissociated and adsorbed in atomic form (step 1). Ethylene and ethane are adsorbed on two adjacent catalytic sites. Step 3 describes the (irreversible) chemical reaction. At this stage of the calculations,  $\text{C}_2\text{H}_5$  radical was not treated as an individual species (see below).

The catalyst surface is represented by a square lattice corresponding to the (100) face of the fcc crystal structure of Pt. Thus each lattice site has four nearest neighbors, referred to as *adjacent sites*. Adsorbed hydrogen atoms are allowed to migrate to adjacent sites only; diagonal movement is not allowed (for details of movement of carbonaceous species, see below).

An important feature of the model is the introduction of the steric hindrance parameter showing how many carbon atoms are allowed to be adsorbed on sites adjacent to an adsorbed carbon atom. For ethylene and ethane, this can vary between one and four (one is the lowest possible value to allow the other carbon atom of the molecule to be adsorbed). Possible events include adsorption of hydrogen or ethylene; surface movement of hydrogen atom, ethylene, or ethane; reaction between two hydrogen atoms and ethylene; association of two hydrogen atom (necessary condition for hydrogen desorption); and desorption of ethylene, ethane, and hydrogen.

Reaction occurs instantaneously if species to react occupy adjacent sites. In other words, whenever the right constellation occurs (there are at least two hydrogen atoms on the six sites adjacent to an ethylene), reaction takes place unconditionally. For simplicity, and to keep the number of the adjustable parameters to a minimum, we did not introduce the ethyl radical ( $\text{C}_2\text{H}_5\cdot$ ) as an individual species. However, a surface constellation consisting of an ethylene and a single hydrogen atom on a site adjacent to it can be considered as an ethyl radical. Practically all processes involving the ethyl radical (except for its surface movement, which should be of minor importance) are represented in our model; the hydrogenation of ethyl radical corresponds to the case when another hydrogen atom appears on a site adjacent to the ethylene, and dissociation into ethylene and hydrogen atom corresponds to the case when either the hydrogen atom or the ethylene moves away from the other. Finally, if two hydrogen atoms occupy adjacent sites, a hydrogen molecule may

desorb (governed by the desorption probability of hydrogen).

## The Program

Flow charts of the program are shown in Figures 1–4. In these figures, the symbol r.n.g. indicates that the corresponding block employs the random number generator. The random number generators used in different blocks are all independent (i.e., use different starting seeds) to facilitate reproduction or debugging, if necessary. Figure 1 illustrates the organization of the program.

### INPUT

The following parameters can be set (either manually or automatically in using the program as part of a parameter-estimation algorithm).

- size of the matrix representing the catalyst surface
- probabilities of 1) hitting the surface (calculated from the pressure of hydrogen and ethylene), 2) sticking to the surface (for hydrogen molecule and ethylene), 3) movement on the surface (for hydrogen atom, ethylene, and ethane), 4) desorption from the surface (for hydrogen molecules, ethylene, and ethane)
- value of the steric hindrance parameter (to facilitate future development, each species may have a different steric hindrance parameter)

- length of the simulation (total number of events to be simulated)
- frequency at which kinetic properties [such as surface coverage of the various species as well as turnover frequency (TOF<sup>9</sup>)] have to be reported

### DRIVER

The “bookkeeping” is done in this block. The occupancy table and the count of reactive events are updated, and the surface coverage is calculated for each species (the latter is needed for calculations of some of the possible events). TOF is calculated as the ratio of reactive events over the number of hits by hydrogen molecules. The latter serves as an internal clock; the number of hits per unit time on a given surface at given pressure and temperature can be calculated from the Boltzman equation<sup>8</sup> (see below).

The block contains a subroutine to allow observation of the catalyst surface on the computer screen during calculations. By using the occupancy table, different symbols are put on the computer screen for each catalytic site corresponding to the status of that particular site (i.e., whether empty or occupied, in the latter case indicating also the species being adsorbed). Insofar as only those points at which a change occurred have to be updated, the activation of this subroutine does not slow the computation considerably.

### CHOICE OF THE ELEMENTARY EVENT

The possible events are hitting on the surface (by hydrogen or ethylene), diffusion (movement) on the surface (by hydrogen atom, ethylene, or ethane), and desorption from the surface (by hydrogen, ethylene, or ethane). The probabilities of diffusion and desorption are calculated taking account of the surface coverage; the other probabilities have fixed values (see above under Input). With relative probabilities of the events held constant, the probabilities are normalized so that the sum of the probabilities gives one. The justification for this approach is given below under Results and Discussion. A call of the random number generator decides which event will take place.

### OUTPUT

The output produced at predetermined intervals consists of the characteristic values (surface coverage for each species, number of reacting

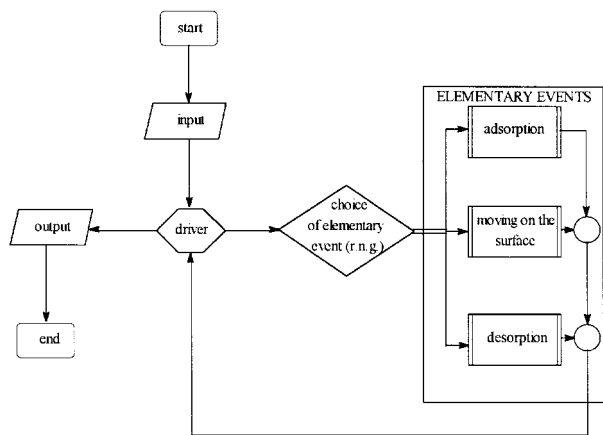


FIGURE 1. Flow chart of the program.

events, TOF), followed by the occupancy table. The latter may be useful for postsimulation statistical evaluation.

Figure 2 shows the organization of the subroutine simulating the hitting of the surface by a molecule. First, the sites to be hit (two adjacent surface sites in each case) are chosen. Sites must be empty and, in the case of ethylene hitting, must not be hindered (i.e., adjacent sites occupied by sterically hindered molecules may prevent adsorption, depending on the steric hindrance parameter and on the surroundings of the molecule already on the surface). Not every hit on empty, accessible sites results in adsorption; the sticking probability embodies energetic considerations and decides whether or not the hit results in adsorption. Because hitting by hydrogen serves as an internal

clock, the number of hits (whether resulting in adsorption or not) is recorded.

As a general rule, after a change in the occupancy, the possibility of reaction occurring is checked (naturally, after desorption, no such check is performed). Only one reaction may occur after each change in the occupancy; however, there might be more alternative partners for a reaction, and in such cases one has to choose randomly from the possible partners.

Figure 3 shows the organization of the subroutine simulating the diffusion of a surface species. Hydrogen atoms move whenever the randomly chosen new site (adjacent to the original site) is empty. A carbon atom has only two possible sites to which to move the two sites adjacent to the fixed carbon of the same molecule, which are in

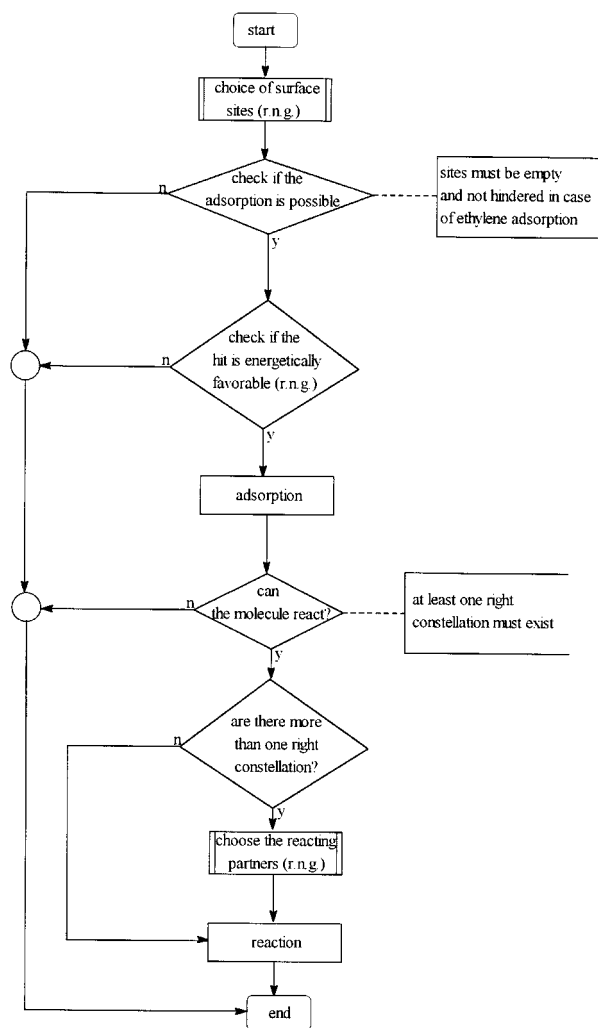


FIGURE 2. Flow chart of the subroutine for adsorption.

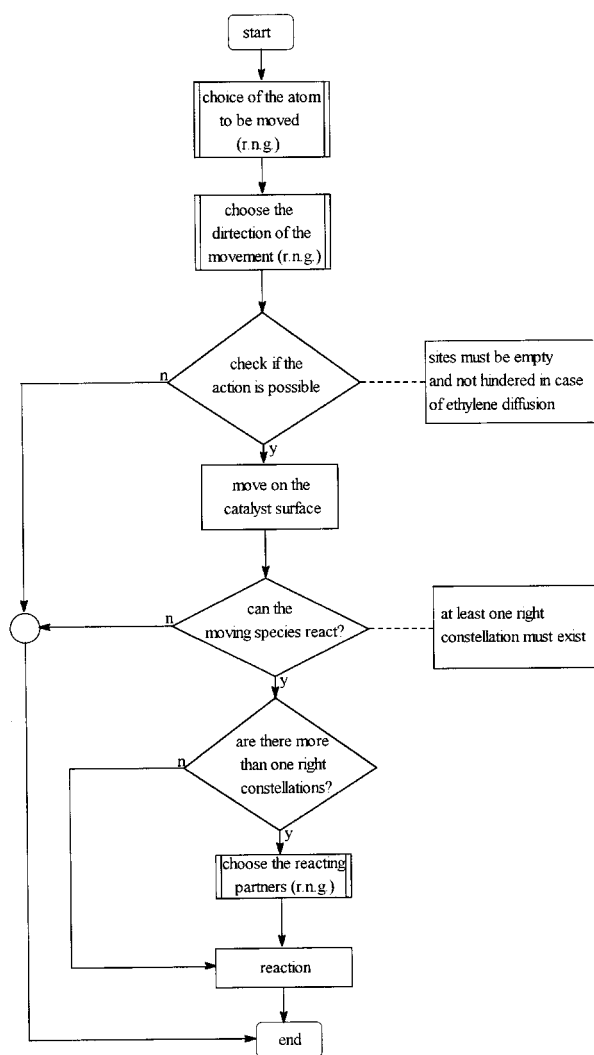


FIGURE 3. Flow chart of the subroutine for diffusion.

positions diagonal to the original site occupied by the moving carbon atom. Naturally, the new site must be empty, but even then steric hindrance can prevent a carbon movement. If the chosen movement cannot be realized, the subroutine is abandoned. After a successful movement, the possibility for the reaction to occur is checked as outlined above.

Figure 4 shows the organization of the subroutine simulating desorption from the surface. Desorption of ethylene or ethane is straightforward; the molecule is picked randomly, and the occupancy table is adjusted. For hydrogen atoms, the procedure is more complicated. A single hydrogen atom is chosen randomly, and adjacent sites are checked for occupation by a hydrogen atom. If at least one adjacent site is occupied by a hydrogen atom, then desorption of a hydrogen molecule occurs (if there are more than one possible partners, the partner is chosen randomly). If there is no hydrogen at adjacent sites, the subroutine is ended.

## Results and Discussion

Before using the model for description of the experimental findings, two sets of test runs were made. The first set was designed to validate our

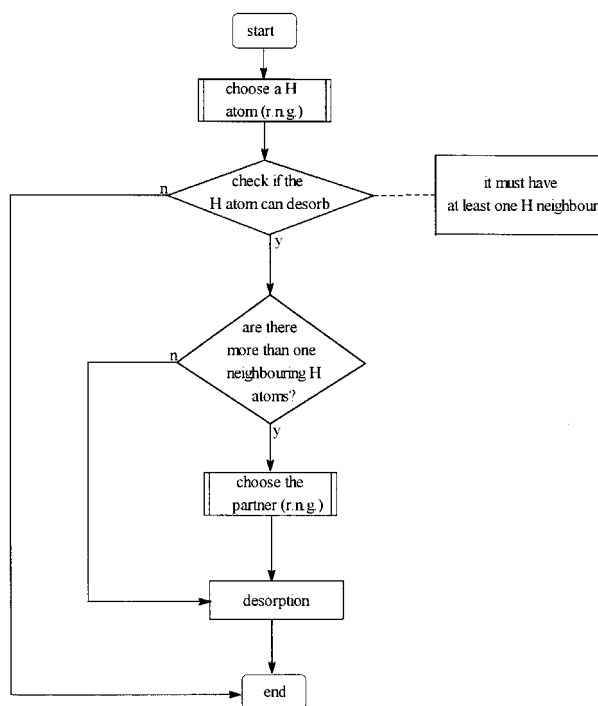


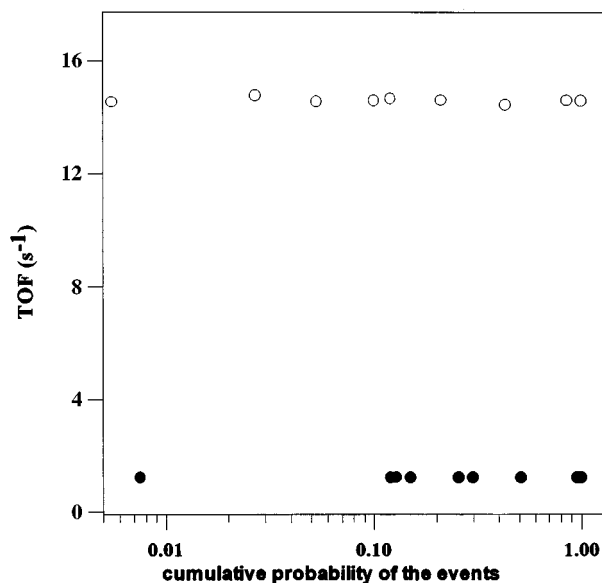
FIGURE 4. Flow chart of the subroutine for desorption.

approach of normalizing the sum of the probabilities of all possible events to one.

In the original MC concept, a very small time slice is chosen, so small that the probability of simultaneous events is negligible (i.e., the sum of the probabilities of all events should be kept below 0.1 in order to have the probability of two events occurring simultaneously lower than 1%). Consequently, the random number generator and the time-incrementing statement are called much more frequently than events occur. Although this method requires lengthier calculations, it supplies the absolute frequencies of the various events directly. However, another approach is also possible, if only the relative frequencies of the events are required. Normalizing the sum of all events to one (keeping the relative probabilities of the events constant) is equivalent to using time slices so long that, in each time slice, at least one event occurs and considering only the first event to occur in each time slice. This allows calculation of the relative frequency of events only; for conversion to absolute frequencies, an internal clock is needed. In our case, hitting the surface by hydrogen is an ideal internal clock; this is the event with the highest probability (even at low hydrogen pressures), and the absolute frequency of hits can be calculated using the Boltzmann equation.<sup>8</sup>

It can be shown with the help of basic probability theory that the ratio of the frequency of two independent events will be the same, if it is calculated using either of the approaches outlined above. Because we cannot prove that the events on the catalyst surface are independent of each other, we had to perform test runs. With the same set for the probabilities of all events, the length of the time slice has been changed during a set of traditional MC calculations, so that the sum of the probabilities varied from 0.01 to 1. As can be seen in Figure 5, the ratio of reactions to the number of hits by hydrogen is not influenced by length of the time slice (i.e., by the magnitude of the sum of the probabilities of all elementary events). Thus, normalizing the sum of the probabilities of the events to unity is allowable, because we need only the relative frequency of reactive events over the hits on the surface. This makes the calculations much faster (indeed, this makes it possible to use PCs for the task).

Next, we tested the effect of the catalyst matrix size.<sup>10-12</sup> Obviously, catalyst sites on the border of the matrix are not equivalent to sites inside the matrix (border sites do not have the same number of adjacent sites). Owing to complications with

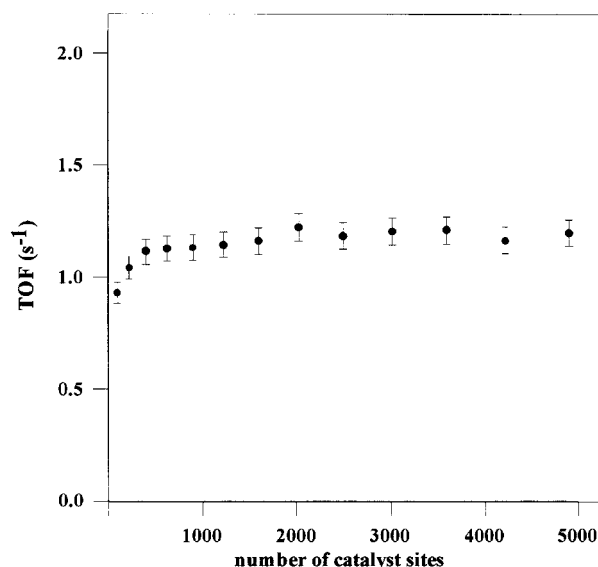


**FIGURE 5.** Ethylene hydrogenation on a (100) surface of Pt catalyst. Effect of changing the length of the time slice, i.e. the sum of probabilities of all possible events on the turnover frequency at different reaction conditions. Solid circles,  $p_{H_2} = 7.6$  kPa,  $p_{C_2H_4} = 3.3$  kPa,  $T = 298$ K; open circles,  $p_{H_2} = 88.4$  kPa,  $p_{C_2H_4} = 3.3$  kPa,  $T = 298$ K.

steric hindrance calculation, the concept of periodic boundary conditions has been not applied. Increasing the matrix size (at the expense of running time) will minimize the influence of border sites. Figure 6 shows the size effect. Although a matrix of approximately  $15 \times 15$  would be large enough, most of the calculations have been performed using a much larger size  $50 \times 50$ , because later we would like to study the effect of catalyst poisoning, for which a considerable catalyst area has to be available.

Typically, the simulation reached steady-state conditions within about  $10^4$  hits by hydrogen. Calculations were usually run for  $2.75 \times 10^7$  hits by hydrogen, and, in order to have sound statistics, we evaluated characteristics (e.g., TOF) averaging values accumulated during the final  $6.25 \times 10^6$  hydrogen hits. The average running time for a simulation ( $p_{H_2}$  ranging between 8 and 80 kPa) lasted for 15 min on a 66 MHz 486 DX IBM PC, 3.5 min on a 133 MHz IBM Pentium, and about 0.5 min on an IBM 3093 200 JVF. (Without normalizing the sum of the probabilities of all events to one, the same numbers were 120 min for the 486 PC and 4 min for the IBM 3093.)

No relevant effects were observed when varying the starting seeds of the different random



**FIGURE 6.** Ethylene hydrogenation on a (100) surface of Pt catalyst ( $p_{H_2} = 7.6$  kPa,  $p_{C_2H_4} = 3.3$  kPa,  $T = 298$ K). Effect of the size of catalyst matrix on turnover frequency.

number generators (less than 1% on the values of the final simulation data). As outlined in the Introduction, our aim has been to interpret laboratory data with the help of the MC simulations. For this purpose, a small part of the data has been used to estimate the adjustable parameters of the model (the probabilities of the various events and the steric hindrance factors). All the remaining laboratory data were used to check the correspondence with the values calculated by the MC simulation.

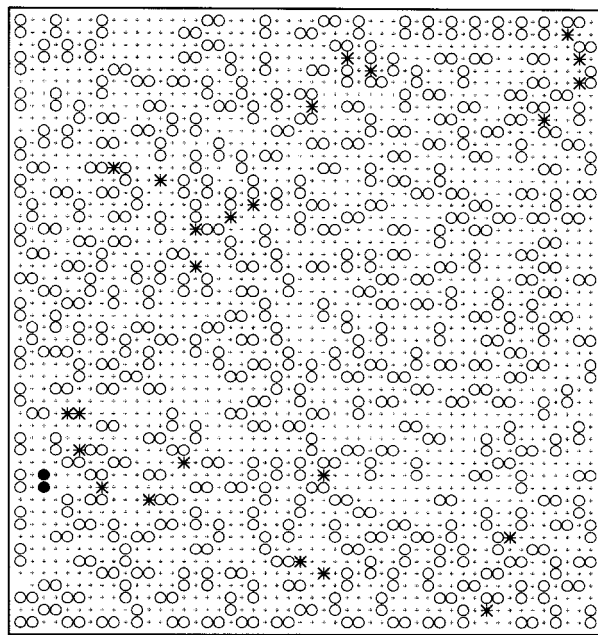
The model is able to describe all experimental findings, as detailed in our earlier work.<sup>8</sup> The model is so robust that using a single TOF vs. hydrogen pressure curve (at fixed ethylene pressure) for fitting the model parameters results in good description of all other TOF vs. hydrogen pressure curves (for different ethylene pressures) and TOF vs. ethylene pressure curves as well. A small change in the model (the introduction of ethyl radical as an individual species, adsorbed on a single site) did not affect the quality of the description of the experimental results. The parameter values were within physically meaningful limits. The only parameter for which there is no background literature data is the steric hindrance parameter governing the maximal allowable number of carbon atoms on adjacent sites. The parameter estimation routine used to calculate the best fit for the experimental curve chosen was very sensitive to this parameter. Only the lowest possible

value (one) gave results consistent with experimental observations (in the case of higher values not only was the difference between calculated and observed points greater but even the shape of the curve did not follow the experimental trend). It must be emphasized that the model gave plausible explanations for unusual experimental findings, such as TOF vs. ethylene pressure curve, which goes through a maximum at very low ethylene pressures.

Some results of the modeling were unexpected; e.g., coverage of the catalyst surface was somewhat lower than estimated. To examine the catalyst surface visually during the reaction, we added a subroutine providing a mapping of the catalyst surface on the monitor during calculations. Because only the changes in the occupancy matrix had to be updated, this did not slow the calculation considerably. The catalyst sites were marked with different symbols according to their occupancy. The speed of calculations on a PC with a 486 CPU running at 66 MHz resulted in a vividly moving picture, which could be monitored effortlessly. In looking at these pictures, it became evident that, although the surface coverage (fraction of occupied catalyst sites) was fairly low (around 0.4), there was little room left for the adsorption of ethylene (which requires two unhindered adjacent sites). The majority of the events involved hydrogen (adsorption, movement, and desorption). Ethylene (and ethane) seemed to be almost motionless compared to hydrogen; i.e., in most cases reaction was caused by the movement of hydrogen. Though the real usefulness of such a visual aid is in its rapidly changing nature, a sample picture is shown in Figure 7. As can be seen from the figure, the surface coverage for ethylene was only 21%, but careful examination of the residual free surface reveals that only 47 more ethylene molecules could be accommodated on the surface (less than 10% of ethylene adsorbed). Taking into consideration that ethylene hits the surface at random, it is not surprising that the ethylene coverage is so low.

## Conclusions

With the help of the model reaction of ethylene hydrogenation on platinum, we have shown that MC modeling is a useful and widely applicable tool in the study of alkene hydrogenation on metal catalysts and, more generally, of catalytic processes. It is a good and relatively simple test of our



**FIGURE 7.** "Snapshot" of the (100) Pt catalyst surface at steady-state conditions ( $p_{H_2} = 7.6$  kPa,  $p_{C_2H_4} = 3.3$  kPa,  $T = 298$  K). Small dots, empty sites; open circles, ethylene carbon atoms; solid circles, ethane carbon atoms; asterisks, hydrogen atoms.

hypothesis regarding the microscopic events taking place on the catalyst surface. Its use is not limited to modeling existing experimental data; based on such modeling, good estimates can be obtained for experimental conditions that are unpractical or impossible to attain in the laboratory. By changing various model parameters, it is possible to understand the effect of these parameters on the experimentally observable reaction, which might help in catalyst development. The possibility of visual presentation of the ever-changing catalyst surface during the reaction is an additional help in understanding the key features of the process. Because the running time is relatively short even on a PC, the method can be applied routinely in the laboratory, and this approach can be used as a building block to construct hydrodynamic MC models of the catalyst bed.

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